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SHOCK TUBE STUDIES OF FORMALDEHYDE PYROLYSIS.(U)

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PROJECT SQUID

TECHNICAL REPORT UMO-3-PU

SHOCK TUBE STUDIES OF FORMALDEHYDE PYROLYSIS

by

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APRIL 1978



Project SQUID is a cooperative program of basic research relating to Jet Propulsion. It is sponsored by the Office of Naval Research and is administered by Purdue University through Contract N00014-75-C-1143, NR-098-038.

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Technical Report UMO-3-PU

PROJECT SQUID

A COOPERATIVE PROGRAM OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

CONTRACT N00014-75-1143 NR-098-038

(6) SHOCK TUBE STUDIES OF FORMALDEHYDE PYROLYSIS

BY

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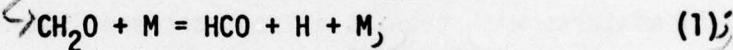
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SUMMARY

Formaldehyde decay was followed by IR emission at $3.5 \mu\text{m}$ behind reflected shocks at total concentrations near 2.4 and $4.5 \times 10^{18} \text{ molecule/cm}^3$. Data were obtained at $0.5 \mu\text{s}$ intervals over a temperature range of 1700-2710 K for mixtures containing 0.1%, 0.5%, and 1.0% CH_2O in Ar. Exponential decay was observed in all cases; at lower temperatures there was evidence of an induction time prior to the onset of the decay. An apparent rate was defined as $k_{\text{a}} = -[d(\ln \text{signal})/dt]/[M]$; k_{a} was observed to be first order in argon and to decrease with increasing dilution.

* micrometers

These data were analyzed in terms of the mechanism:



Using literature values for k_2 , k_3 , and k_4 , a reasonable fit to all the data, both in terms of temperature and concentration dependence, was obtained with $k_f = 6.0 \times 10^{-7} \exp(-364 \text{ kJ/RT}) \text{ molecule}^{-1} \text{ s}^{-1}$. Evidence is also presented to suggest that the reaction

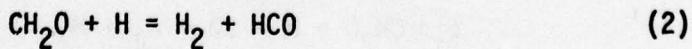
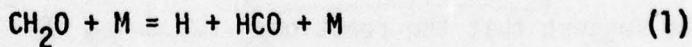


does not play a significant role in the high temperature pyrolysis of formaldehyde.

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INTRODUCTION

Formaldehyde has long been recognized as an important intermediate in many oxidation systems. Furthermore, several recent studies have suggested that the dissociation of formaldehyde is a particularly important reaction in such systems. For example, Peeters and Mahnen¹ reported this reaction to be rate-determining in CH₄/O₂ flames. In a similar vein, the sensitivity analysis of Boni and Penner² indicated that formaldehyde dissociation was one of the four most important reactions in a typical shock tube study of methane oxidation. In spite of its importance, there have been only two high temperature studies which have focused directly upon this reaction. The first, by Gay, et al.,³ measured formaldehyde decay in 2-5% mixtures with neon as diluent between 1530-2100 K. In these experiments exponential decay of formaldehyde was observed after an induction period. The reaction appeared to be first order in neon, and the activation energy for the observed rate constant was 116±10 kJ/mole. Isotopic scrambling was observed when equimolar mixtures of CH₂O and CD₂O were used. This observation, coupled with the presence of an induction period, led these workers to suggest a variety of mechanisms involving hydrogen atom intermediates. One such mechanism was:



The main difficulty here was that this mechanism, analyzed via steady-state assumptions, predicted an activation energy for the observed rate constant in excess of 209 kJ/mole, much higher than that observed. Other mechanisms proposed

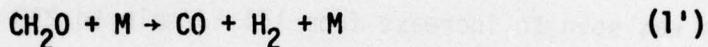
also had certain objectionable features, and it was not possible to assign rate constants to the various elementary reactions. Probably the most salient feature of this investigation was the convincing evidence that secondary reactions played a major role. Thus the rate constant for reaction (1) was appreciably smaller than the observed rate constant for CH_2O decay.

Schecker and Jost⁴ studied the pyrolysis in argon diluent between 1400-2200 K. Here the distinctive feature was use of a variety of CH_2O mole fractions; these ranged from 0.02% up to 1%. Qualitatively, these data were similar to the earlier work--exponential decay with induction periods at lower temperatures. The activation energy was seen to increase from 144 kJ/mole to 230 kJ/mole as the CH_2O mole fraction decreased from 1% to 0.02%. It is important to note these two shock tube studies, with completely different diagnostics, yielded raw data in reasonably good agreement with each other. For example, at 1800 K, Gay, et al., reported an apparent rate constant of $3.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for their 2-5% mixtures, whereas Schecker and Jost reported a value of 1.2×10^{-15} for their 1% mixture. The dilution study would suggest that a somewhat higher value would be expected for the more concentrated case. Furthermore, the Schecker-Jost values were obtained at ten to eighty times higher total concentrations. Thus part of the remaining discrepancy may be due to the fact that, at the higher concentrations, reaction (1) is no longer in the low-pressure region for a unimolecular dissociation reaction. If this were the case, the primary dissociation would not be quite as rapid as calculated at the higher pressures; this could be reflected in a lower apparent decay rate. In any event, it would appear the data is reasonably consistent.

Schecker and Jost analyzed their data in terms of the mechanism given above

and reported values for the various rate constants. The one troubling aspect of this analysis is the observation that the activation energy for the 1% mixtures, even though ~ 30 kJ/mole higher than that reported by the earlier workers, is still quite low to be consistent with the results of a steady state analysis of the mechanism listed above.

The situation with respect to formaldehyde dissociation became considerably more confused as a result of the CH_4/O_2 flame studies of Peeters and Mahnen.¹ Here the data were interpreted to indicate that formaldehyde dissociated directly to molecular products:



with $k_1' = 3.5 \times 10^{-8} \exp(-146 \text{ kJ/RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In addition to the obvious difference in the mechanism of dissociation, this study suggests a dissociation rate at 1800 K some three orders of magnitude larger than the total decay rate measured in the shock tube work.

The present study was initiated to attempt to clarify the formaldehyde decay process. Here an extensive numerical integration study was coupled to the traditional data reduction techniques. Thus the effects of the secondary reactions could be determined without resorting to approximate schemes such as the steady-state assumption. Furthermore, this approach allows one to properly account for the temperature changes that invariably occur in such a system. It was also possible to extend the temperature upwards to 2700 K. Analysis of this new data in this way suggests that the scheme outlined by Gay, et al., is quantitatively consistent with the observations, but that the rate constant assignments of Schecker and Jost must be modified. Perhaps, most importantly, this study

presents additional evidence that reaction (1') must have a rate constant many orders of magnitude lower than that reported in the literature.

EXPERIMENTAL

The 7.6 cm shock tube, gas handling system, and optical configuration have been described previously.⁵ Infrared emissions were first collimated by two slits 1.5 mm wide and 5.0 mm high placed 50 mm apart. Emissions then passed through either a 3.50 μm interference filter (FWHM = 0.12 μ) or a filter wheel set at 3.50 μm (FWHM = 0.15 μ) and were focused upon a liquid-nitrogen-cooled indium antimonide detector. The 3.50 μm emission should be due exclusively to CH_2O . The formyl radical, a proposed intermediate, has its band centered near 4.02 μm .⁶ The detector-preamp combination had a nominal rise time of 1 μs . Output from the preamp was collected by a Biomation Model 805 transient recorder at 0.2 or 0.5 μs intervals. The interference filter was used for the most dilute mixture; the larger transmittance here meant that all of the data exhibited similar S/N characteristics.

Formaldehyde was prepared by heating paraformaldehyde to $\sim 100^\circ \text{C}$, passing the distillate through a dry ice-acetone trap, and then condensing the monomer at 77 K. Care was taken to keep the monomer pressure below 1 kPa (7.5 torr) at all times to minimize polymerization. The monomer was then subjected to several bulb-to-bulb distillations from dry ice to liquid nitrogen temperatures. Then, while at -78°C , it was distilled into the mixing bulb. In most cases a fresh batch of CH_2O was prepared for each mixture. The argon was Airco Research Grade (99.9998%) and was used without further purification.

The shock tube was typically pumped down to $\sim 3 \text{ mPa}$ and the observed leak-outgassing rate was usually near 4 mPa/min. The tube was isolated from the pumps for approximately one minute prior to shock initiation; the nominal background

pressure was near 7 mPa. Since the test section was pressurized to 1.4-2.7 kPa with the mixtures of interest, the background impurities from the shock tube were present in the low ppm range in the shocked mixtures. Mylar diaphragms and helium driver gas were used throughout.

Temperatures behind the reflected shock were computed in the usual way from measured incident shock velocities. Reflected shock pressures were measured with a fast response pressure transducer and were always found to be in good agreement with those calculated. Furthermore, the reflected shock pressure was always constant over the time interval that data were collected; as a result, no attempt was made to correct for non-ideal effects.

RESULTS

The mixtures studied are listed in Table I. Mixtures A and B were prepared from the same formaldehyde batch, whereas all the other mixtures were prepared from separate batches. In most cases, the $3.50 \mu\text{m}$ signal decayed exponentially after an initial rapid rise upon shock front passage. At lower temperatures there was evidence of an induction period prior to onset of decay, and this phenomenon was more evident for the most dilute mixture. A typical experimental record is shown in Fig. 1. Each experiment was characterized in terms of its exponential decay by an apparent rate constant k_a ($k_a \equiv -\{d(\ln \text{signal})/dt\}/M$) where M was the total concentration. Values of these apparent rate constants are listed in Table I. Note in the Table that half of the experiments for mixture A were done at total concentrations nearly a factor of two lower than all the other shocks. Values of k_a there fell in nicely with all the other 1% data. This suggests the decay is first order in argon, and this observation is consistent with that of Gay, et al., who worked at comparable number densities. All of the data with $M \sim 4.5 \times 10^{18} \text{ molecules cm}^{-3}$ are plotted in Fig. 2. There is no evidence (cf. Table I) of variation in k_a with different mixtures of the same $\text{CH}_2\text{O}/\text{Ar}$ ratio, and in Fig. 2 mixtures are grouped together. Note in Fig. 2 the decrease in k_a as the system becomes more dilute. The error bars shown are for one standard deviation, and it is evident the shift is not simply a statistical aberration. This trend is reinforced by another sequence of experiments with a 0.2% $\text{CH}_2\text{O}/\text{Ar}$ mixture. These data are not reported due to larger than normal temperature uncertainties resulting from a malfunction of a velocity gauge. However, these data are consistent with the trend seen, particularly with respect to the decrease in

k_a at lower temperatures in more dilute systems. The Arrhenius parameters corresponding to the least-square lines in Fig. 2 are listed in Table II. Note that the trend of increasing E_a upon dilution is qualitatively consistent with that observed by Schecker and Jost. The values observed here for k_a compare favorably to those reported by the other shock tube workers; at 1800 K, the present values fall between those reported earlier. The most significant difference here is the higher value of E_a for 1% mixtures; note this value is over 50 kJ/mole larger than that reported by Schecker and Jost.

DISCUSSION

Although there are minor differences among the three shock tube studies, as a group they present convincing evidence that the pyrolysis of formaldehyde is a complex process. The observed induction periods, dilution effects, and isotopic scrambling all suggest that secondary reactions play a major role here. A mechanism consisting of reactions (1) - (4) was suggested by earlier workers, and various attempts were made to check the consistency of this scheme with the data collected in this investigation. Following the earlier workers, application of the steady-state assumption to both hydrogen atoms and formyl radicals yields:

$$k_a = k_1 [1 + (k_2 k_3 / k_1 k_4)^{1/2}] \quad [A]$$

This analysis would suggest that the observed activation energy should lie within the range $(\frac{1}{2})(E_{a_1} + E_{a_3})$ (for $k_2 k_3 \gg k_1 k_4$) and E_{a_1} (for $k_2 k_3 \ll k_1 k_4$). For the former case, it was assumed that the activation energies of k_2 and k_4 were negligibly small relative to k_1 and k_3 . Assuming the activation energies are comparable to the bond energies, this analysis would lead to an observed activation energy between ~ 210 kJ/mole and ~ 370 kJ/mole. Although the experimental values are compatible with this lower limit, especially when it is recognized that k_1 and k_3 may have somewhat lower activation energies since these dissociation reactions are occurring in the low pressure region, note that Eq. [A] predicts that there will be no change in k_a upon dilution. This prediction is in marked contrast to the observations. This inconsistency does not necessarily invalidate the mechanism; the problem may well be the steady-state approximations used in the analysis.

It was felt a much better way to test this mechanism would be to numerically

integrate the system of rate equations and compare the calculated profiles to those observed. In addition to allowing one to avoid such assumptions as the steady-state approximation, this approach allows one to accurately treat the variation in temperature which accompanies the pyrolysis. Neglect of such variations could be particularly troublesome here where reaction (1) has a large enthalpy change; the problem is exacerbated by the varying dilutions used.

The procedure employed was straightforward; calculations, using a program previously described,⁷ were done at several temperatures for the various mixtures. The calculated $[CH_2O]$ -time profiles were treated in the same manner as the experimental data. Values of k_a calculated for a specified initial temperature could then be compared to those observed. Results of several representative calculations are shown in Table III. The line labeled C1 used the values of k_1 and k_3 reported by Schecker and Jost⁴; k_2 was taken from the recent work of Klemm,⁸ and k_4 was the value used by Bowman.⁹ Note that the calculated k_a values are much too high here. Results of attempts to lower k_a by using the much lower k_3 value of Bowman⁹ are shown in line C2. Note such a low value of k_3 completely suppresses the dilution effect seen both in this work and in that of Schecker and Jost. It is evident that simple variation of k_3 is not sufficient to reconcile the calculated and observed results.

Of the three remaining rate constants, k_1 would appear to be the most poorly defined. Reaction (2) has been carefully studied,⁸ at least at lower temperatures, and reaction (4) is known to be very fast even at room temperature.¹⁰ Equation [A] suggests k_a is at least as sensitive to k_1 as any other rate constant. In this light, a series of calculations were done where k_1 was varied while the other rate constants were fixed. Here the Schecker-Jost value was used for k_3 .

to preserve the observed dilution effect. This value is similar to that recently reported by Jachimowski,¹¹ but larger than that obtained by Tsuboi.¹² A reasonable fit to all the data, both in terms of temperature and concentration dependence, was obtained with $k_1 = 6.0 \times 10^{-7} \exp(-364 \text{ kJ/RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. These results are shown in line C3 of Table III. This activation energy seems slightly high for a unimolecular dissociation in the second order region. Using a recent ΔH_f° value for the formyl radical,⁶ $\Delta E_a = 371 \pm 10 \text{ kJ/mole}$ for reaction (1). Troe's¹³ analysis of low pressure dissociation reactions would suggest an activation energy near 320 kJ/mole for reaction (1) with this ΔE_a . However, use of lower activation energies for k_1 in the calculations failed to give agreement with the 0.1% mixture data. It was possible to use lower activation energies by increasing the temperature dependence of the secondary reactions. Here the most plausible increase involves k_2 , since k_3 already has an activation energy equal to its endothermicity and k_4 is expected to have very little temperature dependence. An example of the type fit that could be obtained is shown in line C4 of Table III. Note that a better fit could have been obtained with a slightly larger pre-exponential term for k_1 , but such fine tuning was considered unnecessary. This adjusted k_2 is equal to Klemm's value at 1800 K and is 1.5 times larger than Klemm at 2500 K. It appeared that no real improvement was afforded by modifying k_2 . The simpler method of varying only k_1 seemed preferable, particularly in light of the obvious uncertainty in k_1 .

The effects of varying k_3 and k_4 were checked by separately changing these rate constants by a factor of two. Such a change caused a shift of $\sim 25\%$ in k_a for the 1% mixtures at 1800 K. For other conditions, the shift was smaller; particularly significant was the observation that these changes had virtually

no effect upon k_a for the 0.1% mixture. Thus, k_a only depends upon the values of k_1 and k_2 here. In essence then, the fitting procedure consisted of adjusting k_1 to fit the observations on the 0.1% mixtures. With this fit, it was then found that good agreement could be obtained for the more concentrated mixtures using literature values of the other rate constants. Furthermore, given the fact that k_a for these more concentrated mixtures was reasonably sensitive to the values used for the rate constants of these secondary reactions, the fit obtained suggests these literature assignments are reasonably accurate. Of course, the disclaimer must be added that the calculations only indicate the overall effect, and that it is certainly possible that some error in k_3 has been offset by a corresponding error in k_4 .

This assignment of k_1 was based exclusively upon comparisons of the exponential decay of CH_2O in the mixtures with concentrations near 4.5×10^{18} molecules/ cm^3 . Additional calculations, using the rate constants of C3, were done at 2.3×10^{18} molecule/ cm^3 . Values of k_a obtained for the 1% mixtures here were in good agreement with those at the higher concentrations; this was consistent with the experimental observations. A final set of calculations was used to check the entire $[\text{CH}_2\text{O}]$ -time profile. Here the purpose was to use the C3 rate constants, which gave good fits to k_a , to see if these values were also able to describe the early time behavior in the experiments. At the higher temperatures and correspondingly short reaction times, the observed emission signal is affected by the finite slit width as well as the response time of the detector. To account for these factors the calculated concentration-time profile was first corrected for the 1 μs detector response time; this modified concentration-time profile was then integrated over a trapezoidal slit function. The detector efficiency

was assumed to be unity for the 1.5 mm slit width and then drop linearly to zero at a distance 2.0 mm beyond each slit edge. Here t_0 was defined as the time at which the reflected shock was first visible to the detector. Typically, t_0 was 5 μ s earlier than the arrival of the shock front at the slit midpoint. Results of such a calculation are shown in Fig. 1. The fit appears to be quite reasonable; note that a shift of the calculated values by $\sim 1\mu$ s would noticeably improve the fit. Such a shift is compatible with the estimated 1-2 μ s uncertainty in locating t_0 . Fits comparable to that shown in Fig. 1 were also observed at the higher temperatures. At lower temperatures, the reaction times were sufficiently long that slit effects can be neglected. It is in this region that the data suggest an induction period prior to the onset of exponential decay. Comparison of profiles in this region again indicated good agreement. Particularly satisfying was the fact that the calculations showed the same variation of induction time with mixture dilution that was seen experimentally. In summary, the rate constant combination C3 appears to accurately model all aspects of the observed CH_2O decay. In retrospect, it would appear that the failure of Eq. [A] to account for various aspects of the data was not due to a deficiency in the mechanism; the problem was obviously related to the mechanistic analysis via the steady-state assumption.

A comparison of the rate constant for formaldehyde dissociation to the total rate constant for decay gives one an estimate of the importance of the secondary reactions in formaldehyde pyrolysis. The ratio k_1/k_a ranges from $\sim 1\%$ for 1% mixtures at 1800 K to $\sim 40\%$ for 0.1% mixtures at 2500 K. This variation is also mirrored in the product distribution. At the lower temperatures, the calculations indicated that $[\text{H}_2]/[\text{H}] \gg 1$ once there had been any appreciable decay of

CH_2O . At 2500 K this ratio is somewhat higher than unity for 1% mixtures, but becomes much less than unity for the 0.1% mixture. It is interesting to note that the product distribution from the chain decomposition mechanism may often resemble that expected if the dissociation were to go directly to molecular products, i.e., reaction (1').

The observed rates of formaldehyde decay in all of the shock tube experiments suggest that the k_1' rate constant assignment from the CH_4/O_2 flame work¹ is much too large. At 1800 K, the shock tube results indicate a total decay rate constant of $\sim 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, whereas $k_1' = 2 \times 10^{-12}$ at this temperature. Furthermore, the shock tube work suggests that secondary reactions play a major role in the decay scheme. Thus, decay of CH_2O via reaction (1') must have a rate constant much lower than k_a , and the present work suggests that the total decay can be adequately modeled without inclusion of reaction (1'). It would appear that the molecular dissociation path is not a significant reaction channel in the high temperature pyrolysis of formaldehyde.

REFERENCES

1. Peeters, J. and Mahnen, G.: Fourteenth Symposium (International) on Combustion, p. 133, Combustion Institute, 1973.
2. Boni, A.A. and Penner, R.C.: Comb. Sci. and Tech. 15, 99 (1977).
3. Gay, I.D., Glass, G.P., Kistiakowsky, G.B., and Niki, H.: J. Chem. Phys. 43, 4017 (1965).
4. Schecker, H.G. and Jost, W.: Ber. Bunsenges. Physik. Chem. 73, 521 (1969).
5. Dean, A.M. and Steiner, D.C.: J. Chem. Phys. 66, 598 (1977) and references therein.
6. Chase, M.W., Curnutt, J.L., Hu, A.T., Prophet, H., Syverud, A.N. and Walker, L.C.: J. Phys. Chem. Ref. Data 3, 311 (1974).
7. Dean, A.M.: J. Chem. Phys. 58, 5202 (1973).
8. Klemm, R.B.: Rate Parameters for the Reactions of CH₂O with H and O over the Temperature Range 250-470 K. Paper presented at the Fall 1977 Meeting of the Eastern States Section of the Combustion Institute.
9. Bowman, C.T.: Fifteenth Symposium (International) on Combustion, p. 869, Combustion Institute, 1975.
10. Hochanadel, C.J. and Sworski, T.J.: The UV Spectrum and Reaction Kinetics of the Formyl Radical. Paper presented at 175th National Meeting of the American Chemical Society, Anaheim, California, March 1978.
11. Jachimowski, C.J.: Comb. and Flame 29, 55 (1977).
12. Tsuboi, T.: Japan J. Appl. Phys. 15, 159 (1976).
13. Troe, H.: J. Chem. Phys. 66, 4758 (1977).

TABLE I.

SUMMARY OF EXPERIMENTAL OBSERVATIONS

<u>Mixture</u>	(a) <u>T/K</u>	<u>M/10¹⁸ molecule cm⁻³</u> ^(b)	<u>k_a/10⁻¹⁶ cm³ molecule⁻¹ s⁻¹</u> ^(c)
A 1.01% CH ₂ O	2545	4.77	1010
	2350	4.62	426
	2175	4.48	201
	2065	4.37	121
	1970	4.28	77.3
	1945	4.24	49.8
	1885	4.21	32.8
	1795	4.11	20.0
	2710	2.45	1630
	2700	2.45	1180
B 1.01% CH ₂ O	2585	2.42	1620
	2540	2.40	792
	2470	2.40	812
	2385	2.33	700
	2275	2.28	391
	2220	2.31	302
	2510	4.73	791
	2465	4.69	595
C 1.00% CH ₂ O	2330	4.59	410
	2250	4.54	359
	2150	4.46	156
	2505	4.74	747
	2445	4.59	564
	2390	4.68	568
	2385	4.68	385
	2280	4.62	271
	2270	4.51	332
	2220	4.50	178
D 0.50% CH ₂ O	2055	4.33	115
	1970	4.33	46.4
	1925	4.19	32.7
	1830	4.16	21.0
	1810	4.17	22.5
	1700	3.98	8.77
	2010	4.26	54.5
	2005	4.24	49.7
	2005	4.27	48.8

TABLE I. (Continued)

<u>Mixture</u>	(a) <u>T/K</u>	<u>M/10¹⁸ molecule cm⁻³</u> (b)	<u>k_a/10⁻⁶ cm³ molecule⁻¹ s⁻¹</u> (c)
E 0.51% CH ₂ O	2435	4.62	740
	2380	4.58	434
	2255	4.46	197
	2160	4.41	151
	2040	4.25	76.5
	1960	4.19	42.0
	1845	4.08	26.5
	1765	4.01	12.2
F 0.10% CH ₂ O	2595	4.63	410
	2480	4.57	444
	2475	4.54	379
	2350	4.47	257
	2300	4.45	188
	2220	4.37	87.9
	2190	4.30	73.7
	2085	4.30	39.3
	2030	4.19	28.2
	1930	4.11	17.1
	1855	3.95	10.8
	1790	3.95	5.57

(a) Balance of all mixtures was argon.

(b) Total concentration.

(c) $k_a \equiv -(d \ln (\text{Signal})/dt)/M$.

TABLE II. LEAST SQUARE PARAMETERS FOR k_a

<u>Mixture</u>	<u>$\ln A^{(1)}$</u>	<u>$\sigma(\ln A)$</u>	<u>E_a (kJ/mol)</u>	<u>$\sigma(E_a)$</u>	<u>$\sigma(\ln k_a)$</u>
1% (A,B,C)	-20.69	0.267	197.4	4.7	0.16
0.5% (D,E)	-20.24	0.601	208.3	10.2	0.19
0.1% (F)	-20.18	0.495	222.1	8.8	0.20

(1) Units of A are $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$.

TABLE III. COMPARISON OF CALCULATED AND OBSERVED
VALUES OF $k_a^{(1)}$

	0.1% CH ₂ O		0.5% CH ₂ O		1.0% CH ₂ O	
	1800K	2500K	1800K	2500K	1800K	2500K
Observed ⁽²⁾	6.09 ± 1.20	390 ± 77	14.7 ± 2.8	725 ± 136.	19.4 ± 3.1	778 ± 124
C1	26.9	676	46.6	1140	51.0	1440
C2	6.57	548	6.60	594	6.49	578
C3	7.07	349	14.6	652	16.2	808
C4	6.27	294	13.9	594	15.2	752

RATE CONSTANTS FOR CALCULATIONS

	$k_1^{(3)}$		k_2		k_3		k_4	
Set	$\ln A$	E_a	$\ln A$	E_a	$\ln A$	E_a	$\ln A$	E_a
C1	-16.3	301	-23.9	16.0	-22.1	61.4	-21.8	0
C2	-16.3	301	-23.9	16.0	-25.5	79.4	-21.8	0
C3	-14.3	364	-23.9	16.0	-22.1	61.4	-21.8	0
C4	-16.1	339	-22.4	37.6	-22.1	61.4	-21.8	0

(1) Units are $10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(2) Error bars are $\pm\sigma$.

(3) A in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, E_a in kJ/mol.

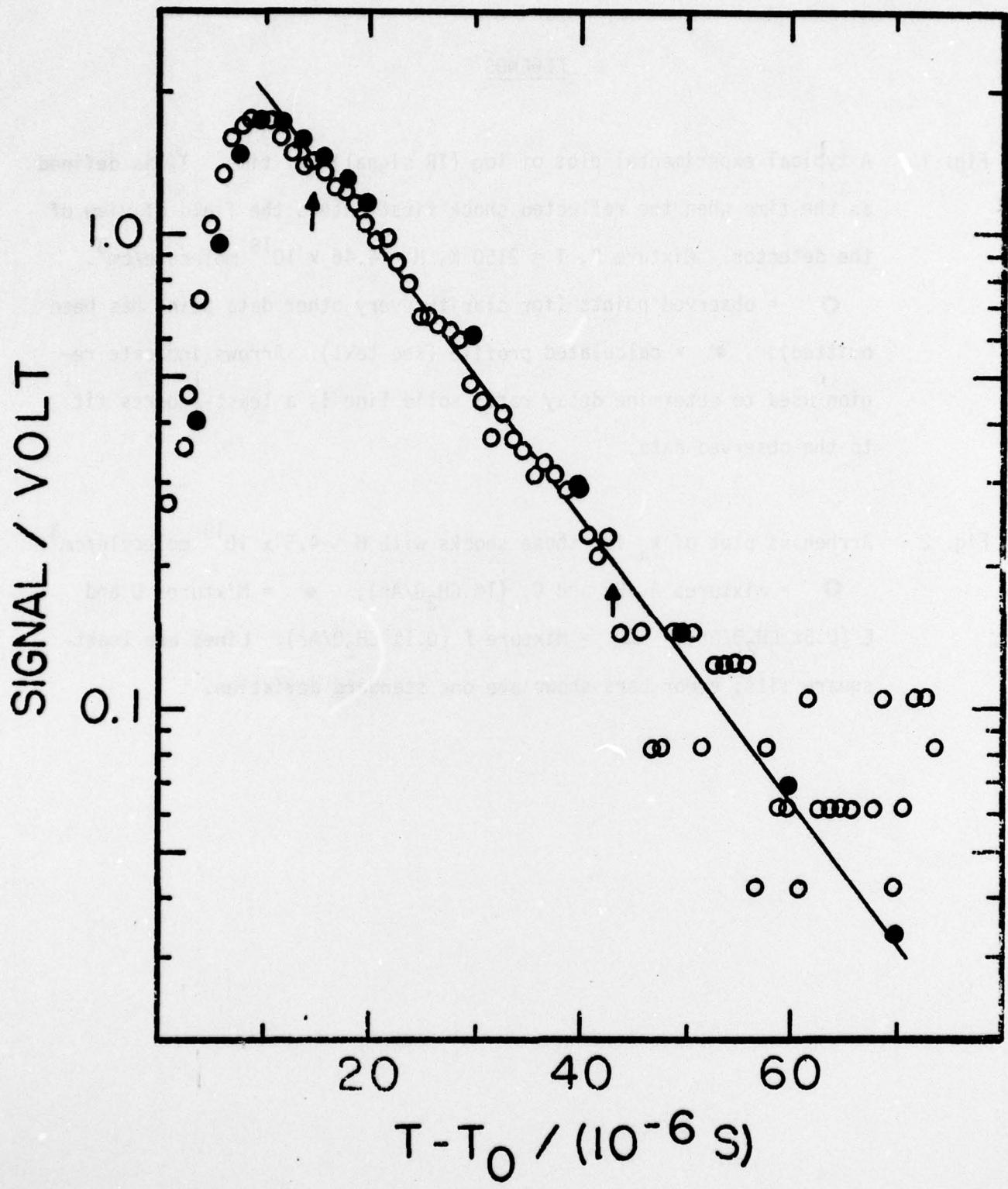
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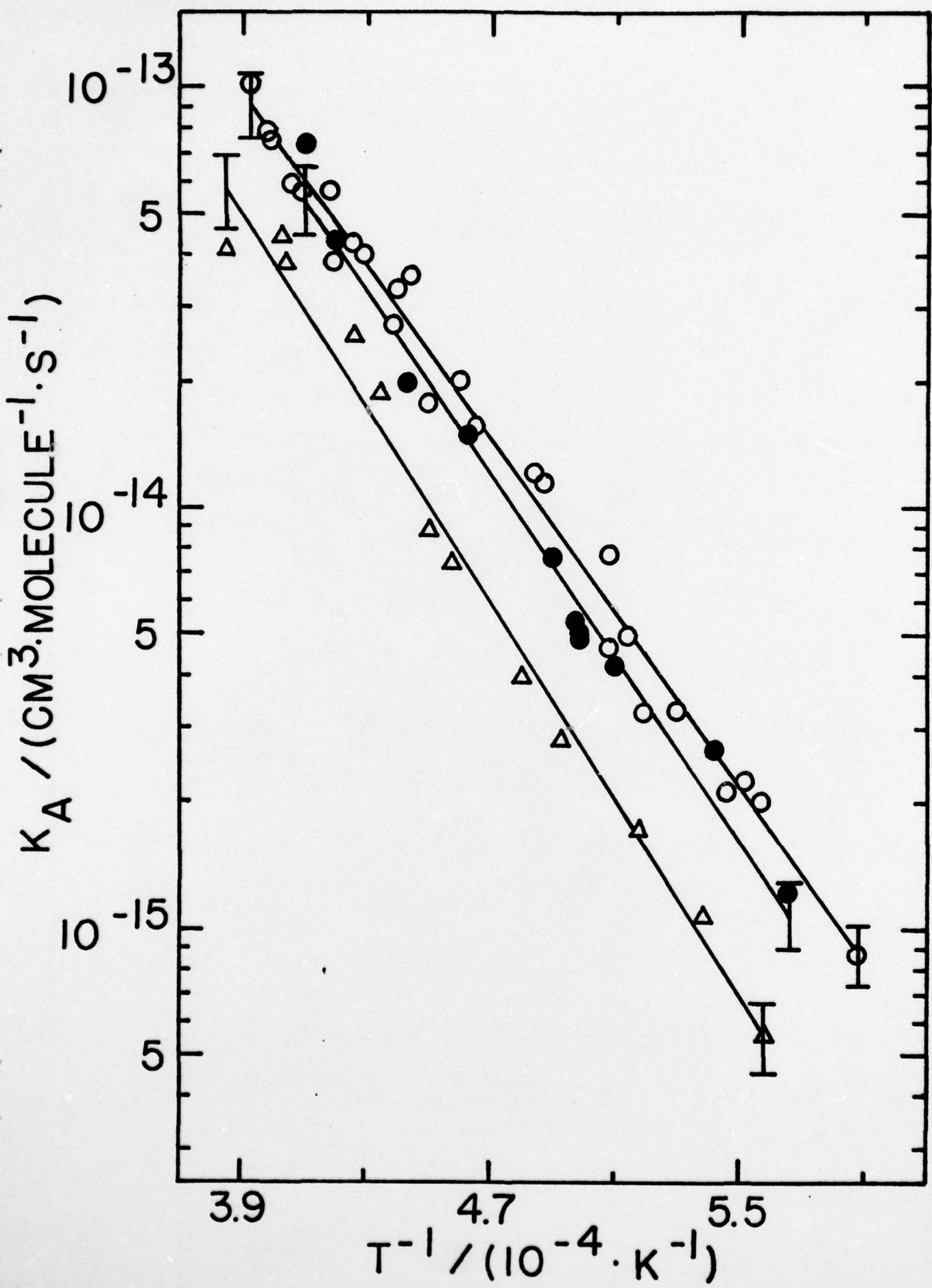
Fig. 1 A typical experimental plot of log (IR signal) vs. time. T_0 is defined as the time when the reflected shock first enters the field of view of the detector. Mixture B, $T = 2150$ K, $M = 4.46 \times 10^{18}$ molecule/cm³.

○ = observed points (for clarity every other data point has been omitted); ● = calculated profile (see text). Arrows indicate region used to determine decay rate; solid line is a least-squares fit to the observed data.

Fig. 2 Arrhenius plot of k_a for those shocks with $M \sim 4.5 \times 10^{18}$ molecule/cm³.

○ = mixtures A, B, and C. (1% CH₂O/Ar); ● = Mixtures D and E (0.5% CH₂O/Ar); △ = Mixture F (0.1% CH₂O/Ar). Lines are least-square fits; error bars shown are one standard deviation.





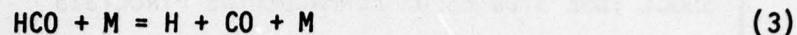
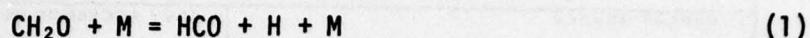
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER UMO-3-PU✓	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SHOCK TUBE STUDIES OF FORMALDEHYDE PYROLYSIS		5. TYPE OF REPORT & PERIOD COVERED Technical-Scientific
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Anthony M. Dean, Brian L. Craig, Ron L. Johnson, M. Claire Schultz and Edward E. Wang		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-1143✓
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dept. of Chemistry University of Missouri-Columbia✓ Columbia, Missouri 65201		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-098-038
11. CONTROLLING OFFICE NAME AND ADDRESS Project SQUID Headquarters✓ Chaffee Hall Purdue University, West Lafayette, IN 47907		12. REPORT DATE April 1978
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Office of Naval Research, Power Program Code 473 Department of the Navy 800 No. Quincy Street Arlington, VA 22217		13. NUMBER OF PAGES 24
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; its distribution is unlimited.		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Same		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Shock Tube Studies Formaldehyde Pyrolysis		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Formaldehyde decay was followed by IR emission at $3.5\mu\text{m}$ behind reflected shocks at total concentrations near 2.4 and 4.5×10^{18} molecule/cm ³ . Data were obtained at 0.5 μs intervals over a temperature range of 1700-2710 K for mixtures containing 0.1%, 0.5%, and 1.0% CH ₂ O in Ar. Exponential decay was observed in all cases; at lower temperatures there was evidence of an induction time prior to the onset of the decay. An apparent rate was defined as $k_a = -[d^*kb \text{ signal}]/dt]/[M]$; k_a was observed to be first order in argon and to decrease with increasing dilution.		

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These data were analyzed in terms of the mechanism:



Using literature values for k_2 , k_3 , and k_4 , a reasonable fit to all the data, both in terms of temperature and concentration dependence, was obtained with $k_1 = 6.0 \times 10^{-7} \exp(-364 \text{ kJ/RT}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Evidence is also presented to suggest that the reaction



does not play a significant role in the high temperature pyrolysis of formaldehyde.

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